



Production of renewable hydrogen by aqueous-phase reforming of glycerol over Ni–Cu catalysts derived from hydrotalcite precursors

Pablo V. Tuza, Robinson L. Manfro, Nielson F.P. Ribeiro, Mariana M.V.M. Souza*

Escola de Química, Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, Sala 206, CEP 21941-909, Rio de Janeiro/RJ, Brazil

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ABSTRACT

Ni–Cu catalysts derived from hydrotalcite-like compounds were prepared and evaluated in aqueous-phase reforming of glycerol. The catalysts were characterized by chemical composition, textural analysis, crystalline structure and reducibility. The reaction was carried out in a batch reactor with solution of 10 wt.% glycerol, at 250 and 270 °C. A maximum glycerol conversion of 60% was achieved at 270 °C. In the gas phase, the H₂ selectivity was always higher than 80% and formation of CO was very low (<3%) at 250 °C. The addition of Cu decreased the formation of methane. H₂ is consumed during the reaction at 270 °C, mainly for Cu-containing catalysts, with simultaneous formation of propylene glycol in the liquid phase. Acetol, lactic acid and acetaldehyde were also formed in the liquid phase, at both temperatures.

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1. Introduction

Renewable energy sources are becoming increasingly important because of depleting of petroleum reserves and mounting environmental concerns associated with fossil fuel utilization. In this sense, the use of hydrogen as an alternative energy carrier has been largely encouraged over the last years. Nowadays nearly 95% of the world hydrogen is produced from fossil fuels [1], thus, it is necessary to find renewable sources to produce hydrogen. Biomass is a promising source for hydrogen production due to the carbon neutral nature with environmental benefits.

Gasification and steam reforming have been widely investigated for conversion of biomass to hydrogen, but these processes involve high temperatures and many side reactions, which decrease the hydrogen selectivity [2,3]. Aqueous-phase reforming (APR) for production of hydrogen, first developed by the Dumesic group [4], is an advantageous technology for feedstocks such as sugars, alcohols and polyols, because it is carried out at low temperatures, reducing the cost of the process and minimizing undesirable decomposition reactions. Moreover, it produces H₂ and CO₂ in a single reactor with low levels of CO, which is important for fuel cell applications [5].

Several biomass-derived oxygenated compounds have been used in APR process, such as methanol, sorbitol, glycerol, ethylene glycol, and ethanol [4–9]. Glycerol is of particular interest because

it is obtained as a by-product of biodiesel production by transesterification of vegetable oils or animal fats. The transesterification reaction produces approximately 110 kg of glycerol per ton of biodiesel [10]. With increase in production of biodiesel, an excess of glycerol is expected in the world market and therefore, it is essential to find useful applications for glycerol. One of the promising ways to utilize this diluted glycerol from biodiesel plants is to produce hydrogen. The hydrogen generation by APR of glycerol takes place according to the Eq. (1):



Noble metal catalysts are commonly used to carry out the APR at small scales because they are more active and less susceptible to carbon deposition than non noble metal catalysts [6–8]. However, large scale reforming processes use Ni-based catalysts that are far cheaper and more available than noble metals. A good catalyst for APR process has to be active in the cleavage of C–C bonds and water-gas shift reaction, but has to inhibit the cleavage of C–O bond and methanation reactions [4–6,11].

Ni shows a good activity for C–C scission, but it also exhibits high rates of methanation [5]. Cu, on the other hand, is inactive for C–C bond cleavage but has high activity for water-gas shift reaction, thus favoring the selectivity to hydrogen. In the present work Ni and Cu were selected to be included in catalyst formulations applied to glycerol reforming in order to obtain high activity and selectivity to hydrogen.

Hydrotalcite-like compounds (HTLCs) or layered double hydroxides, also known as anionic clays, have a lamellar structure

* Corresponding author. Tel.: +55 21 25627598; fax: +55 21 25627596.
E-mail address: mmattos@eq.ufrj.br (M.M.V.M. Souza).

with alternating positively charged mixed metal hydroxide sheets and negatively charged interlayer anions along with water molecules [12]. Thermal treatments of HTLCs give a stable, high surface area, homogeneous mixture of oxides with very small crystal size, which by reduction results in high metallic dispersion. Ni–Mg–Al mixed oxides prepared from hydrotalcite precursors have been successfully used as catalysts for various reactions, including reforming and oxidation of methane [13–15] and ethanol reforming [9,16]. On the other hand, hydrotalcite-derived Cu–Mg–Al catalysts exhibit high activity for water-gas shift reaction [17]. To our knowledge, Ni–Cu–Mg–Al catalysts derived from hydrotalcites have not been investigated in APR of glycerol yet.

In this context, the objective of this work is to study Ni–Cu catalysts prepared from hydrotalcite precursors in aqueous-phase reforming of glycerol for hydrogen production. The effect of the Cu loading (0–20 wt%) on the catalytic activity for reforming reaction and hydrogen selectivity was investigated, correlating with structural and morphological properties of the catalysts. By-products formed in liquid phase were identified and the main reaction routes were proposed.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-like compounds were prepared by coprecipitation method at room temperature. An aqueous solution containing appropriate amounts of nitrate precursors ($Al/(Ni + Cu + Mg + Al) = 0.25$ and $[Ni + Cu + Mg + Al] = 1.5$ M) was added dropwise to a vigorously stirred solution containing Na_2CO_3 and $NaOH$ ($CO_3^{2-}/Al^{3+} = 0.375$ and $OH^-/Al^{3+} = 6.3$). The gel formed was aged for 18 h at 60 °C. The resulting solid was filtered, washed with distilled water (70 °C) until pH 7 and dried overnight at 100 °C.

The Ni,Cu,Mg,Al-mixed oxides were produced by calcination of HTLCs under flowing air (60 mL min⁻¹), using a heating rate of 10 °C min⁻¹, from room temperature to 500 °C and keeping at this temperature for 2 h.

The NiO loading in calcined samples was always 20 wt% and CuO loading was varied between 0 and 20 wt%. The samples will be referred to as Ni, Ni5Cu, Ni10Cu and Ni20Cu, according to CuO loading.

2.2. Catalyst characterization

The chemical composition of the synthesized samples was determined by X-ray fluorescence (XRF) using a Rigaku (RIX 3100) spectrometer.

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku Miniflex II X-ray diffractometer equipped with a graphite monochromator using $CuK\alpha$ radiation (40 kV). The measurements were carried out with speed of 2° min⁻¹ and over the 2θ range of 5° and 90°.

The textural characteristics, such as BET specific area and pore volume (BJH method), were determined by N_2 adsorption-desorption at -196 °C in a Micromeritics ASAP 2000. Prior to the analysis the samples were outgassed for 24 h at 200 °C.

The reducibility of the catalysts was analyzed by temperature-programmed reduction (TPR), carried out in a microflow reactor operating at atmospheric pressure. The samples were firstly dehydrated at 150 °C under flowing Ar before the reduction. A mixture of 1.53% H_2/Ar flowed at 30 mL min⁻¹ through the sample, raising the temperature at a heating rate of 10 °C min⁻¹ up to 1000 °C. The outflowing gases were detected by thermal conductivity detector (TCD).

2.3. Catalytic tests

The reactions of APR of glycerol were carried out in an autoclave batch reactor of 600 mL with 450 rpm of agitation, using 400 mg of catalyst in 250 mL of 10 wt.% glycerol solution. Before the reaction, the reactor was purged with He to remove the air inside. The catalytic tests were performed at 250 and 270 °C, resulting in autogeneous pressures of 38 and 52 atm, respectively.

The catalysts were reduced *ex situ* under 75 mL min⁻¹ of 20% H_2/N_2 up to 1000 °C, using a heating rate of 10 °C min⁻¹.

Gas products were analyzed online by gas chromatography (GC-1000), equipped with a Haysep D column and TCD. The products detected in the gas phase were H_2 , CH_4 , CO_2 and CO . The selectivity to these products was calculated based on total moles produced in the gas phase, without considering water.

In the liquid phase glycerol and by-products were quantified by a Shimadzu HPLC with Aminex HPX 87H column, using 0.005 M H_2SO_4 as eluent at 0.6 mL min⁻¹, and both UV and refractive index detectors. Conversion was calculated based on the moles of glycerol in the feed. Some liquid by-products were identified by gas chromatography-mass spectrometry (GC-MS) using a Shimadzu QP2010 instrument with DB5 column.

3. Results and discussions

3.1. Catalyst characterization

The chemical composition of the synthesized samples is presented in Table 1 and Table 2. The composition of the as-synthesized samples is similar to those of the gel of synthesis, indicating an approximately complete incorporation of the cations in HTLC structure. The nickel loading of the sample without copper is slightly lower than the nominal value, which can be due to a small loss of nickel during washing.

The XRD patterns of HTLC precursors (Fig. 1A) exhibit characteristic planes of a well-crystallized HT in carbonate form (JCPDS 41-1428). The absence of other phases suggests that both Ni^{2+} and Cu^{2+} have isomorphically replaced Mg^{2+} cations in the brucite-like layers [9,18,19]. A clear improvement in the orderliness of the layer was noted with decreasing copper content, as indicated by both the increase in intensity and sharpness of (110) and (113) reflections, observed around 60 and 62°, respectively. This effect was expected due to Jahn-Teller distortion at higher concentrations of copper, leading to poor long-range ordering [20].

The lattice parameters a (cation–cation distance in the brucite-like layer) and $c = 3c'$ (thickness of one brucite-like layer and one interlayer) were calculated based on the rhombohedral structure of hydrotalcites, as shown in Table 1. The lattice parameter a increases with copper content since the ionic radius of Cu^{2+} (0.73 Å) is larger than that of Mg^{2+} (0.65 Å) [19]. There is also a decrease of the parameter c with increasing copper content, which can be

Table 1

Chemical composition, structural and textural characteristics of the as-synthesized samples.

Sample	$Al/(Ni + Cu + Mg + Al)^a$ (molar)	a (Å)	c (Å)	S_{BET} (m ² /g)	V_{PORE} (cm ³ /g)
Ni	0.26 (0.25)	3.053	23.59	46.4	0.106
Ni5Cu	0.28 (0.25)	3.055	23.49	42.1	0.167
Ni10Cu	0.25 (0.25)	3.059	23.29	60.5	0.152
Ni20Cu	0.24 (0.25)	3.064	23.20	62.0	0.145

^a The values in parentheses are nominal values.

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